Decisive Role of a Phenyl Group at the α-Position of Benzoylacetone in the Solvent Extraction of Al^{3+} and In^{3+}

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Al^{3+} is readily extracted into benzene with α-phenylbenzoylacetone, while In^{3+} is entirely unextractable, which leads to an efficient extraction-separation of Al^{3+} from In^{3+}.

Al^{3+} and In^{3+} ions are readily extracted with β-diketones such as acetylacetone (AA), benzoylacetone (BA) and thenoyltrifluoroacetone (TTA).[1] Recently, we have reported that the distance between the two donating oxygens in β-diketones affects the acidity of the ligand itself and its ability to separate lanthanides.[2] The present work is a preliminary report on the decisive role of substituent at the α-position of a β-diketone in the solvent extraction of Al^{3+} and In^{3+}, illustrated by benzoylacetone and α-phenylbenzoylacetone (PhBA).

The distances between the two donating oxygens in the neutral (HA) and the anionic (A^-) forms of BA and PhBA were estimated by a semi-empirical MNDO/H† calculation and are listed in Table 1. It can be seen that the O···O distances in PhBA both in the neutral and anionic forms are reduced relative to that in BA owing to steric repulsion between the α-phenyl group and the terminal methyl and phenyl groups. The O···O distances in the anionic forms of BA and PhBA were obtained assuming the enol moiety lies on a plane. The intramolecular hydrogen-bond energy (E_{OH}) can be estimated from the energy difference between the hydrogen-bonded structure and the open structure in which the O–H is rotated by 180° in order to minimize the hydrogen bond energy. These values are also given in Table 1. The value of E_{OH} for PhBA is significantly larger than that for BA owing to the shorter hydrogen bond in the enol moiety. The strong hydrogen bond in PhBA is also detected in the ^1H NMR spectrum. The very sharp signal assigned to the hydroxy proton of PhBA appeared at δ 17.39, whereas that for BA was rather broad and observed at a higher field (δ 16.15). The ^1H NMR spectra also demonstrate that both BA and PhBA exist quantitatively in the enol form in $CDCl_3$, although it has been reported that the presence of a methyl group at the α-position in β-diketones increases the proportion of the keto form.[3] The acid dissociation constants, pK_a, were measured by potentiometric titration in dioxane–water (3 : 1) at 25 °C. It was found that PhBA is a slightly weaker acid than BA.

The extraction of Al^{3+} and In^{3+} into benzene with BA or PhBA has been investigated.‡ The results for PhBA are shown in Fig. 1, where the extraction percentages are plotted against the pH of the aqueous phase. The extraction of Al^{3+} increased with increasing pH and almost 100% of the Al^{3+} was extracted at pH 4.8. On the other hand, extraction of In^{3+} was not seen at all below pH 5; a precipitate which seems to be due to hydrolysis of In^{3+} was observed above pH 5.

In the solvent extraction of tervalent metal ions (M^{3+}) such as Al^{3+} and In^{3+}, the extraction equilibrium and the extraction constant, K_{ex}, can be expressed by eqns. (1) and (2).

$$M^{3+} + 3HA_{org} \rightleftharpoons MA_{3,org} + 3H^+ \qquad (1)$$

$$K_{ex} = [MA_3]_{org}[H^+]^3/[M^{3+}][HA]^3_{org} = D[H^+]^3/[HA]^3_{org} \qquad (2)$$

Subscript org denotes the organic phase and D the distribution ratio of M^{3+}, $[M^{3+}]_{org}/[M^{3+}]$. When log D values are plotted against pH, we obtain straight lines with a slope of 3, indicating that the extracted species are $Al(BA)_3$, $In(BA)_3$ and $Al(PhBA)_3$

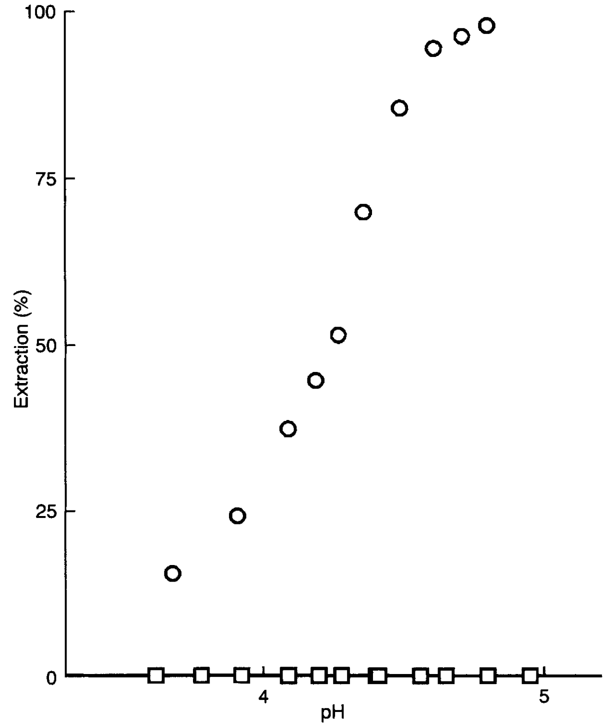
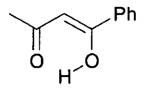
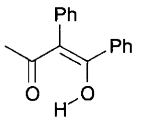


Fig. 1 Extraction of Al (○) and In (□) into benzene with PhBA. Conditions as in Table 2.



Benzoylacetone
(BA)



α-Phenylbenzoylacetone
(PhBA)

Table 1 Comparison of properties of BA and PhBA

	BA	PhBA
O···O distance[a]/Å		
HA	2.51	2.44
A^-	3.10	2.84
E_{OH}[a]/kJ mol^{-1}	63.45	75.62
^1H NMR δ (OH)	16.15	17.39
pK_a[b]	12.66	12.90

[a] Calculated by MNDO/H. [b] Measured in dioxane–water (3 : 1), $[NaClO_4]$ = 0.1 mol dm^{-3}.

Table 2 Extraction of Al^{3+} and In^{3+} with BA and PhBa

	$pH_{1/2}$[a]		log K_{ex}	
	Al	In	Al	In
BA	3.20	3.39	−6.60	−7.17
PhBA	4.24		−9.72	

[a] Organic phase: $[HA]_{org}$ = 0.1 mol dm^{-3} in benzene. Aqueous phase: $[NaClO_4]$ = 0.1 mol dm^{-3}, added to keep the ionic strength at 0.1; $[MeCO_2H]$ = 0.01 mol dm^{-3}, added as a buffer component; $[M^{3+}] = 1 \times 10^{-4}$ mol dm^{-3}. Extractions were performed at 25 °C.

in accordance with eqns. (1) and (2). Log K_{ex} values were obtained from eqn. (2) employing the $pH_{1/2}$ values at which half of the metal ion was extracted ($D = 1$); these were read from the log D *vs.* pH plots and are given in Table 2.

As seen in Table 2, both Al^{3+} and In^{3+} are readily extracted with BA. Owing to its smaller ionic radius, Al is extractable from more acidic media than is In^{3+}. However, generally the separation of Al^{3+} and In^{3+} is difficult since their extraction behaviour is very similar. On the other hand, in the extraction with PhBA, although Al^{3+} was only extracted at rather high pH values, extraction of In^{3+} was not observed at all below pH 5. Consequently, it is possible to separate Al^{3+} from In^{3+} using this ligand. The lower extraction efficiency of Al with PhBA than with BA can be partly ascribed to the lower acidity of PhBA and to steric crowding of the ligands in the resulting complex: with the introduction of the phenyl group in the α-position, the distance between the terminal methyl and phenyl groups increases so enhancing the steric repulsion between the ligands. The effect of steric repulsion on the stability of the complex should be significant, because the ionic radius of Al^{3+} is very small. This aspect requires further examination.§

It is quite interesting that In^{3+} could not be extracted at all with PhBA. An X-ray crystallographic study of aluminium and indium β-diketonate complexes serves to confirm the role of the substituent at the α-position. The O···O distances in $Al(AA)_3$,[4] $In(AA)_3$[5] and $In(TTA)_3$[6] are reported to be 2.726, 2.905 and 2.905 Å, respectively. Since the O···O distance in the indium complex is unusually longer than that in the aluminium complex, it appears that more energy is required for PhBA to rearrange its configuration to accommodate the complex structure relative to BA, and steric repulsion between the α-phenyl group and the terminal methyl and phenyl groups could prevent widening of the two donating oxygens around the metal centre.

In conclusion, we have established an efficient extraction separation system for Al^{3+} and In^{3+}. The decisive role of the α-substituent demonstrated in the present work should be further applicable to the molecular design of organic reagents of high selectivity.

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Footnotes

† This is an MNDO calculation that takes hydrogen bonding into consideration and was performed on fully optimized molecular geometries on a Cray Y-MP2E/264 computer using the MNDO93 program (Cray Research Inc.).

‡ The pH was adjusted by means of hydrochloric acid and sodium hydroxide solutions. The metal concentration in the aqueous phase was determined by inductively coupled argon plasma atomic emission spectrometry. Concentrations in the organic phase were determined similarly after back-extraction with a hydrochloric acid solution.

§ In the extraction of Al^{3+} and In^{3+} with dibenzoylmethane, the extraction of In^{3+} is higher than that of Al^{3+}.[1] This supports the significance of interligand contacts in the Al–PhBA complex.

References

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